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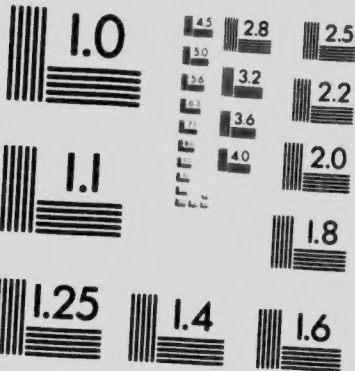
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REPORT No. 5

CANADIAN WASTE SULPHITE LIQUOR AS A SOURCE OF ALCOHOL

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CANADIAN WASTE SULPHITE LIQUOR AS A SOURCE OF ALCOHOL.*

About a year ago, when the manufacture of explosives was in full swing, with no indications of an early ending of the war, Canada was buying millions of gallons of alcohol from companies across the border at a price double that of pre-war days. It seemed to many that this might be an opportune time to start an alcohol industry here in Canada, using waste sulphite liquor as a raw material. The proposition was studied by the Imperial Munitions Board in conjunction with several of the Pulp and Paper companies, and, with the assistance of the Forest Products Laboratories of Canada and the Honorary Advisory Council for Scientific and Industrial Research. At the request of Dr. R. F. Ruttan, Chairman of the Associate Committee on Chemistry of the Advisory Research Council, we made a study of a number of liquors supplied by the mills of Eastern Canada to find out how they compared with the European liquors and those in the United States, as they are already being used for this purpose. The liquors were accordingly tested for acidity, gravity, total solids, ash, organic matter, total sugars, fermentable sugars, and pentoses

As some of the methods used may not be familiar, they will be briefly described. The acidity was determined by a method used by Haegglund[1].

Twenty (20) cc. of the liquor are titrated with tenth normal soda hydroxide until a drop of the solution added to filter paper moistened with an alcoholic solution of phenolphthalein turned slightly pink. The number of cc. of the alkali required represents the number of degrees of acidity. This is not the neutral point as measured by hydrogen ions, but it gives results which can be repeated, and, therefore, a basis of comparison. The results obtained give an excellent basis on which to calculate the amount of lime necessary to reduce the acid sufficiently to make the liquor fermentable. The total solids, ash, pentoses, and organic matter

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were determined by the usual procedure and will, therefore, not be described.

The total sugars were extracted by Krause's[2] method. Fifty (50) cc. of sulphite liquor are placed in a porcelain dish and a slight excess of barium carbonate, necessary to neutralize the acid present, is added. Sand is then added to prevent the residue from forming a hard mass, and the mixture is heated on a water-bath. When the mass becomes a thick paste it is treated with 60 cc. of 90 per cent alcohol. The solution is boiled for 30 seconds with constant stirring. The dish is then removed and the solution allowed to settle. It is then filtered and the process repeated until all the sugar is extracted. The filtrate is transferred to a 500 cc. distilling flask and the alcohol boiled off. The last traces of alcohol are removed with the aid of a suction pump. The residue in the flask is made up to a definite volume and the sugar estimated volumetrically with Fehling's solution, observing the precautions given by Breckler[3] and using ferrous thiocyanate as an indicator[4]. It may be interesting to state that a much more rapid method was four ' which gives fairly good results. This method consists of neutralizing the liquor and titrating it directly into the Fehling's solution, using the ferrous thiocyanate as an indicator, same as before. The ratio of the non-sugar reducing substances to the sugars seems to be fairly constant, consequently, if the values obtained are reduced by ten per cent nearly correct results are obtained. The following table gives the figures for the two methods with the differences:—

TABLE 1.

Direct Titration.				Alcohol Extraction.
2·99	less 10 per cent	2·69		2·77
1·6	"	"	1·44	1·47
2·75	"	"	2·47	2·5
1·87	"	"	1·68	1·67
1·67	"	"	1·5	1·5
1·5	"	"	1·35	1·3
2·18	"	"	1·96	2·02
2·24	"	"	2·01	2·02

The fermentable sugars were determined with a pure culture of Fleischmann's yeast. At the time this report was begun we did not have a culture of yeast accustomed to sulphite liquor, and in order to make our results comparable we continued with Fleischmann's yeast. 100 cc. of the liquor were neutralized with soda to an acidity of 3 degrees. A suitable amount of phosphate

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and peptones were then added and the solutions sterilized at 100° C. When they were cool they were innoculated and kept at 29–31° C. in a thermostat. At the end of four days the solutions were filtered and the sugar again determined, takiag into account the slight concentration of the liquor during the fermentation. The loss in sugar was considered as the amount fermentable. As about 4 per cent of the amount of sugar consumed is converted into glycerine, instead of alcohol, and as 180 grams of sugar produce 92 grams of alcohol, we find that 49 per cent of the fermentable sugars gives us the theoretical production of alcohol.

The results of the analysis are given in Table 2.

TABLE 2.

Sample.	1 Acid Value 20 cc. = cc. N 10 Alkali.	2 Sp. Gravity at 15° C.	3 Total Solids grams per 100 cc	4 Ash grams per 100 cc	5 Org. Matter grams per 100 cc	6 Total Sugars as Glucose, grams per 100 cc	7 Organic matter made up of Sugars, per cent.	8 Fermented Sugars, grams per 100 cc	9 Total Sugars Fermentable, per cent.	10 Alcohol, grams per 100 cc	11 Alcohol, per cent by volume.	12 Pentoses as Xylose, grams per 100 cc
1	11·65	1·027	6·1	0·48	5·63	1·5	26·6	1·12	75·0	0·55	0·70	0·593
†	.....	.....	10·2	....	9·4	2·5	....	1·86	....	0·91	1·15	....
2	6·1	1·016	3·4	0·22	3·18	0·98	30·9	0·65	66·3	0·32	0·41	0·408
†	....	....	10·2	....	9·38	2·9	....	1·95	....	0·95	1·20	....
3	16·8	1·043	10·4	0·66	9·74	2·77	28·4	1·98	70·7	0·97	1·23	1·105
4	33	1·045	10·0	0·75	9·25	2·50	27·2	1·7	68·0	0·83	1·05	0·926
5	15	1·047	10·3	1·20	9·1	1·32	14·4	0·86	65·1	0·42	0·53	0·562
6	16·0	1·046	10·8	0·94	9·86	2·02	20·5	1·39	68·8	0·68	0·86	0·695
7	13·9	1·037	7·9	0·81	7·09	1·47	20·7	0·96	65·3	0·47	0·59	0·587
†	....	....	11	....	....	2·02	....	3·3	....	0·65	0·82	....
8	16·	1·047	10·5	1·34	9·16	1·67	18·2	1·02	61·2	0·50	0·63	0·673
9	....	1·048	11·2	1·07	10·13	2·1	20·7	....	....	....	....	....
10	....	1·048	11·32	1·12	10·20	2·0	19·6	....	....	....	....	....
11	12·6	1·0475	11·0	1·11	9·89	2·07	20·9	1·32	63·..	0·65	0·82	0·731
12	19	1·051	12·34	1·11	11·23	2·02	18·0	1·34	66·3	0·66	0·84	0·673

† Corrected to the average total solids of the other liquors supplied by this mill.

On examing the specific gravity and total solids it seems apparent that samples 1, 2, and 7 had been diluted before they reached the laboratory; consequently, they were corrected in the

more important constituents on the basis of the average total solids of the other liquors supplied by the same mill. The others are fairly uniform so far as these tests are concerned and compare favourably with the tests made in European countries. Ahrens[5] gives 1·0465 for specific gravity; Wichelhaus[6] 1·038; Lindsay and Tollens[7] 1·055; while Walker[8], who investigated Canadian liquors in 1913, recorded 1·05. The total solids recorded in the literature vary over a wider field. Wichelhaus[6] gives 8·28 grams per 100 cc., Lindsay and Tollens[7] gives 9 to 10 per cent, and Seidel[9] 11·44 per cent. As the Canadian liquors also vary from 9 to 11 per cent, they are fully as concentrated as those found in the European mills.

The total sugar content varies from 1·32 to 2·9 grams per 100 cc., if we accept the correction for the liquors which were considered diluted. The one with the lowest sugar content comes from a 17-hour cook, where much of the sugar must have been destroyed through cooking, as the gravity and total solids compare favourably with the other liquors. We also feel that sample 8, with a sugar content of 1·67, is not a representative one, as this same mill in four other liquors examined did not have a content less than 2 grams per 100 cc. It may be interesting to note that the temperature in this cook was from 145 to 155° C. during the last hour, which we will find later on materially decreases the amount of sugar in the liquor. We, therefore, believe that in representative liquors from mills in Eastern Canada the amount of total sugar varies from 2 to 2·9 grams per 100cc. The data in the literature vary over a wide range. Krause[2] gives 1·47 grams per 100 cc. for the Ritter-Kellner cook, while Haegglund[1] gives from 2·4 to 2·9 per cent.

The percentage of the sugars which are fermentable varies from 61·2 to 75 per cent of the total. It is an important fact that those liquors which have the highest sugar content also have the highest per cent of fermentable sugar. Liquor number 8, which we have already pointed out, is low in sugar, due to the high temperature during the last hour, had only 61 per cent fermentable sugar, while those liquors which have over 2·5 grams per 100 cc. of sugar have 66·3 per cent and over fermentable. In other words, if the conditions of the cook are such that the sugars are destroyed, the fermentable ones are the first to go. This is a confirmation of observations made by Haegglund[1].

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The percentage of alcohol by volume (100 per cent alcohol), excepting samples 5 and 8 for reasons already given, varies from 0·82 to 1·23. As about 90 per cent of the alcohol is recoverable in the distillation the liquors should yield from 0·72 to 1·1 per cent in actual practice. The four best liquors would yield on this basis fully 1 per cent. These results compare favourably with those obtained in Europe. Klasson[10] states that the usual yield is 1 per cent. Lindsay and Tollens[11] in 1891, working with liquors from a mill in Aschaffenburg, reported a yield of 0·58 to 0·67 per cent by volume. In 1905 Krause[3] reported a yield of 0·5 to 0·7 per cent by volume. In 1910 Mattheus[12] also reported a yield of 0·7 per cent. In the most recent work of Haegglund a volume of 1 per cent is considered satisfactory under favourable conditions The best Canadian liquors will, therefore, produce as much alcohol as any of those reported in Europe.

When column 7, giving the per cent sugar in the organic matter, is examined, it becomes apparent that the liquors fall into two distinct classes. The one class contains from 26·6 to 30·9 per cent of the organic matter in the form of sugars, while the other class contains only 18 to 20·9 per cent. Or, the first class has from 2·4 to 2·77 per cent of sugar, while the other class has only 1·6 to 2 per cent. Those liquors which are rich in sugars, are rich, therefore, not because they have more wood dissolved in them, but because more of the organic matter which they contain is made up of sugar. It is of considerable interest, to know, from the point of view of production of alcohol from the liquor, why there is this marked difference in sugar content. The records of the cooking in Table 3 do not give any explanation for this difference, as there is little variation in them.

The free acid was slightly less in the liquors rich in sugar, although this alone cannot account for the marked difference between the two series. Sample 5, for instance, had 3·94 per cent free acid and 28·4 per cent of its organic matter in the form of sugars, while sample 10, had 4·03 per cent free acid and only 19·6 per cent of its organic matter in the form of sugars. Haegglund[1] showed that the per cent of sugar in the liquor rises to a maximum and then falls off again. It was, therefore, conceivable that the maximum had been passed in those liquors where the sugar was low. To determine this point we analyzed two series of samples taken from the digester every hour starting with the fifth hour.

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One series was supplied by a mill which produced a high sugar to organic matter ratio, and the other by a mill which gave a relatively lower ratio. The results are given in Tables 4 and 5.

TABLE 3.

Sample.	Length of Cook.	Total Acid.	Combined Acid.	Free Acid.
	Hours.			
1				
2	10	5·06	1·16	3·9
3		5·08	1·14	3·94
4	9	5·15	1·51	3·64
5	17	4·67	1·27	3·4
6	7½	5·28	1·05	4·23
7	8¾	4·57	0·9	3·67
8	7¼	5·31	1·03	4·28
9	8	5·15	1·06	4·09
10	7¾	5·05	1·02	4·03
11	8	6·00	1·40	4·60
12	8½	5·78	1·10	4·68

TABLE 4.

Cook "A."

Time.	Total Solids, grams per 100 cc.	Organic Matter, grams per 100 cc.	Total Sugar, grams per 100 cc.	Sugar, per cent of Total Solids.	Sugar, per cent of Organic Matter.
Hours.					
5	4·5	3·6	0·9	20·	25·0
6	6·36	5·46	1·52	23·9	27·6
7	8·7	7·8	2·25	25·6	28·8
8	9·95	9·05	2·37	23·0	26·2
9·15	10·8	10	2·44	21·8	24·4

|		
Combined Acid	1·25	
Free Acid	4·03	Maximum Temperature not given.
Total Acid	5·28	

TABLE 5.

Cook " B."

Time.	Total Solids, grams per 100 cc.	Organic Matter, grams per 100 cc.	Total Sugar, grams per 100 cc.	Sugar, per cent of Total Solids.	Sugar, per cent of Organic Matter.
Hours.					
5	5·6	4·5	1·17	20·9	26·0
6	8·3	7·2	1·69	20·3	23·4
7	10·7	9·6	2·15	20·1	23·1
7½	10·8	9·7	2·2	20·4	22·6

Combined Acid	1·09	
Free Acid	3·39	Maximum Temperature 145° C.
Total Acid	4·48	

The results are also given in Graphs 1 and 2. It is at once apparent that no maximum in the amount of sugar has been passed in either cook. The rate of production of sugar between the fifth and seventh hours is about the same in both cases, amounting to more than fifty per cent of the total produced. The actual amount of sugar is about the same at the end of the 7th hour, but cook "A" keeps on increasing in sugar, while cook " B " was blown shortly afterwards. No doubt cook " B " would also have increased slightly in sugar content had it been continued as long as the first.

It is obvious from Graph 2 that the incrusting substances on the cellulose are going into solution much faster in cook " B " than in cook "A," in spite of the fact that the free acid is higher in "A" than in " B." The final amount of organic matter which goes into solution is about the same in both cases. It is also significant to note that the last 22 per cent of the organic matter in cook "A" produced only 0·19 grams of additional sugar, while the last 25·5 per cent of " B " produced 0·51 grams of sugar. We feel sure that this is due to temperature being rather high near the end of cook "A," in the light of the data to be presented later on. The percentage of sugar in the organic matter is also lower than in the other liquors supplied by this mill, which points in the same direction. Had this ratio been the same as in former cooks analyzed the amount of sugar per 100 cc. would have been 2·8 grams at least.

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We next estimated the mannin content of the wood and the amount of reducing sugar formed when samples of the woods used in the sulphite digester are hydrolized with dilute hydrochloric acid. The samples were kindly supplied by the Canadian Forest Products Laboratories. They passed through a 60-mesh sieve, but were caught in an 80-mesh. We followed Schorger's method of estimating mannin explicitly. To determine the reducing sugars on hydrolysis we digested the wood as directed by Schorger[13] in his mannin determination. The wood of the above degree of fineness was boiled with hydrochloric acid (Sp Gr. 1·025) for three hours. Then the wood was filtered and washed, the filtrate concentrated and extracted with 90 per cent alcohol, and

GRAPH. 1

ORGANIC MATTER—GRAMS PER 100cc

TIME IN HOURS

GRAPH. 2
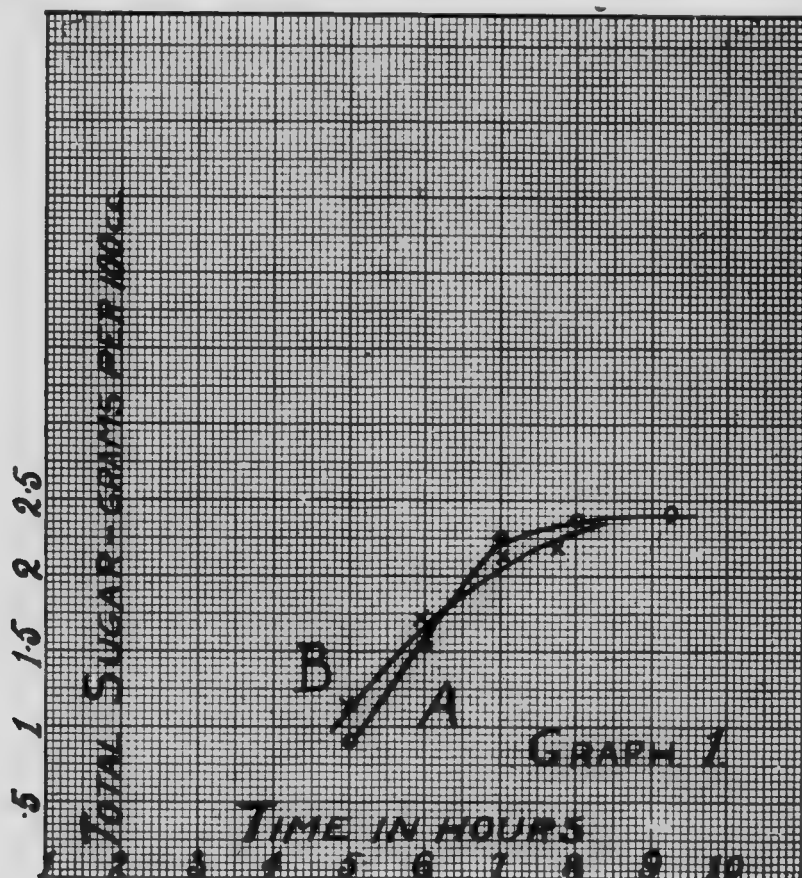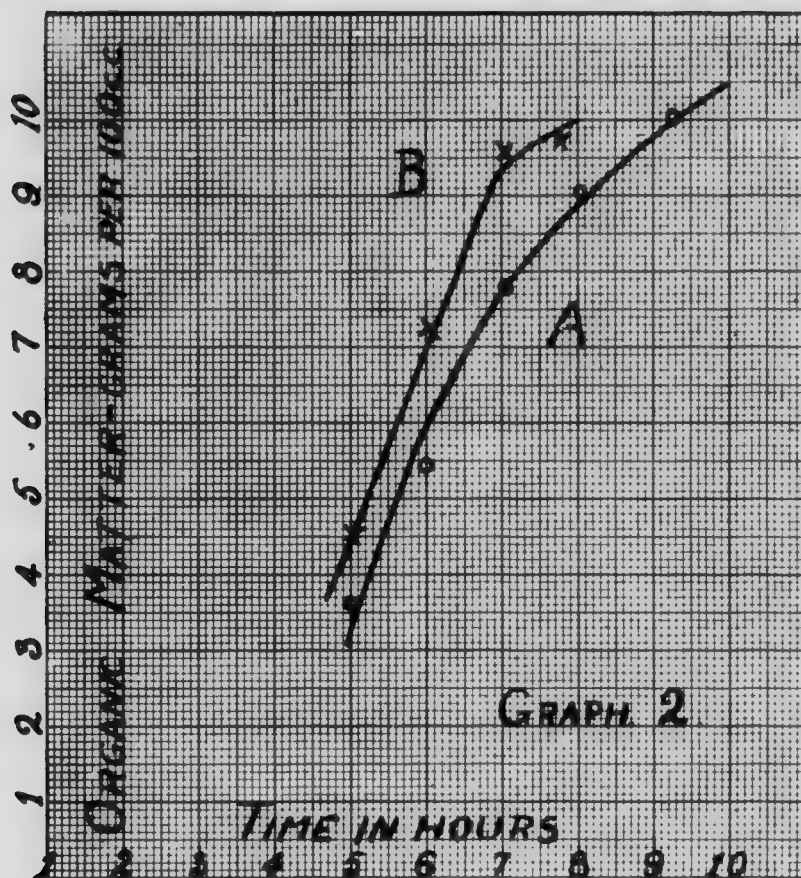
the sugars estimated as already described for sulphite liquor. The results are given in Table 6.

TABLE 6.

	*Mannin, per cent of bone dry wood.	Yield of reducing sugars calculated as hexose, per cent of bone dry wood.
Black Spruce .	6·8	22
Sample taken 2½ feet from ground. annual rings, 119, average diameter, 71-4 inches.		
White Spruce .	7 5	22
Sample taken 2½ feet from ground. annual rings, 107, average diameter, 8 1-16 inches.		
Balsam Fir	7 7	21 1
Sample taken 4½ feet from ground. annual rings, 47, average diameter 7 1-16 inches.		

These results show that there is little difference in the sugar content of the various woods used in the sulphite process and that any marked differences in the liquors cannot be attributed to the species of wood used. The per cent of reducing sugars formed on hydrolysis seems rather high and it is possible that a certain amount of the cellulose is changed to sugar. We did not investigate this possibility, as we were merely interested in finding the relative amount of sugar produced from the three species under the same conditions. Twenty-two (22) per cent of sugar would correspond to a carbohydrate content, having the general formula of $C_6H_{10}O_5$, of the wood of $19\cdot8$ per cent, which is higher than the results usually given by other investigators. It is interesting to see what proportion of these sugars are actually found in our best liquors. As we do not have very accurate data on the volume of liquor in a cook, our figures are only an approximation. It is usually assumed that 5 pounds of water are used for each pound of wood. The total volume for a ton of air dry pulp, or from 4,000 pounds of bone dry wood, would, therefore, be 20,000 pounds. On this basis sample 3, Table 2, would yield 532 pounds of sugar from 4,000 pounds bone dry wood, or $13\cdot3$ per cent of the wood.

Effect of Temperature on Sugar Content.

Mr. Hovey, of the Canadian Forest Products Laboratories suggested that further insight on the formation of sugars might be gained by making two experimental cooks, and offered to make them during his spare time. We were pleased to have the opportunity of examining the liquors and consequently, two cooks were made on pure samples of wood in the experimental digesters of the Forest Products Laboratories. The description of the cooks and the results are as follows:—

SPRUCE COOK.

Weight of wet wood	600	grams
Weight of bone dry wood	463	"
Weight of pulp	271	"
Yield of pulp, $59\cdot5$ per cent. Total time, 11 hours.		
Total volume of liquor	4,640	cc.
Total SO_2	$4\cdot9$	per cent.
Combined SO_2	$1\cdot23$	"
Free SO_2	$3\cdot67$	"
CaO	$1\cdot08$	"

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120 cc. samples were withdrawn through condensers every hour beginning with the 6th hour. The temperature was gradually increased so that it reached 136° C. by the end of the 7th hour. During the next three hours it varied between 136 to 140° C., after which it was raised to 152–155° C. The pressure was also gradually increased and kept between 70–77 pounds after the 7th hour.

TABLE 7.

Time.	Total SO₂ per cent.	Total Sugar, grams per 100 cc.	Total Solids, grams per 100 cc.	Organic Matter, grams per 100 cc.	Sugars x 100 Solids.	Sugars x 100 Organic Matter.
Hours.						
6	3·50	0·46	4·0	1·93	9	18·6
8	2·96	0·86	5·9	3·83	14·5	22·4
9	2·80	0·98	6·8	4·8	14·4	20·4
10	2·58	1·06	7·4	5·4	14·3	19·7
11	1·41	0·88	8·1	6·37	10·8	13·8

BALSAM FIR COOK

Weight of wet wood.... . ...   600 grams
Weight of dry wood................... ....   480 "
Weight of pulp ....   272 "
    Yield of pulp, 56·7 per cent.   Total time, 11½ hours.
Total volume of liquor .. .. 4,600 cc.
Total SO₂ .... 5·38 per cent
Combined SO₂ .... 1·29 "
Free SO₂........................ .... 4·09 "
CaO................................. .... 1·13 "

TABLE 8.

Time.	Total, SO₂ per cent.	Total Sugar, grams per 100 cc.	Total Solids, grams per 100 cc.	Organic Matter, grams per 100 cc.	Sugars x 100 Solids.	Sugars x 100 Organic Matter.
Hours.						
6.	3·52	0·33	4·5	2·36	7·3	14
8	2·55	0·76	6·3	4·16	12·1	18
9	2·2	0·81	7	4·94	11·6	16·3
10	1·73	0·89	7·6	5·6	11·7	16
11½..................	0·75	0·77	7·7	6·34	10	12·1

180 cc. samples were withdrawn every hour after the 6th hour for analysis. The temperature and pressure were the same as in the Spruce cook.

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These results show as well as the results of cook "A" and "B" that 50 per cent of the sugar is formed during a relatively short period of the entire cook, in this case between the 6th and the 8th hour. They also show that the incrusting substances go partly into solution as polysaccharides, which later become hydrolized as the ratio of sugars to organic matter is lower at the end of the 6th hour than at the end of the 8th. After the 8th hour, however, though the actual amount of sugar is still increasing, the ratio of sugar to organic matter is decreasing, which means that some of the sugars are being destroyed. This destruction is especially marked after the 10th hour, when the temperature was raised from 150–155° C. Here the actual amount of sugar decreased in both cases, in spite of the fact that during the previous hour it was still materially increasing. This shows that the actual amount of sugar destroyed was greater than the difference between the final amount present and that present at the end of the 10th hour. The sharp decrease during this period of the ratio of sugar to organic matter illustrates the same point. It, therefore, seems clear that the temperature cannot be increased much above 145° C. without very materially decreasing the amount of sugar present in the liquor.

These analyses also seem to show that Spruce gives more sugar than Balsam, as the ratio of sugar to organic matter is very much higher in the Spruce than in the Balsam, i.e., both cooks have the same amount of organic matter in solution, but the Spruce cook has more sugar. The amount of free acid present in the Balsam cook was less after the 6th hour, as it was necessary to relieve gas in order to keep down the pressure. This apparently did not prevent the incrusting substances from going into solution, but it did slow down the hydrolysis of these substances to sugars. This was proved by hydrolysing the liquor from both cooks at the end of the 9th hour, as well as at the end of the cook with dilute hydrochloric acid, and then estimating the sugars again. The same amount of sugar, relative to the amount of wood used, was now present. This confirms our previous analysis of Spruce and Balsam that the amount of sugar present is about the same in both cases.

This suggested to us that the reason why samples 6 to 12, Table 2, had such a small amount of their organic matter in the form of reducing sugar, might, perhaps, be due to the presence of

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polysaccharides. We, therefore, hydrolysed a number of liquors with 5 per cent hydrochloric acid for 30 minutes, and then neutralized them and estimated the sugars again.

TABLE 9.

	Total Sugars, grams per 100 cc.	Total Sugar after hydrolysis, grams per 100 cc.
Sample 3, Table 2	2·77	2·8
Sample 7, Table 2	1·47	1·61
Sample 9, Table 2	2·1	2·25
Sample 12, Table 2	2·02	2·25
Cook "A," Table 4	2·44	2·68
Cook " B," Table 5	2·2	2·34

With the exception of the first one, they all increase in sugar from 8 to 10 per cent. Consequently, the reason that liquors 6 to 12, Table 1, are low in sugars relative to organic matter cannot be explained by incomplete hydrolysis of polysaccharides, but must be due to the destruction of sugars during the cook. Just what conditions are primarily responsible we are not prepared to say, as not all the mills supplied us with complete data in regard to their cooks, and we did not have the time to make cooks on the laboratory scale to determine them, beyond the marked effect which temperature plays.

In conclusion, I wish to express my indebtedness to Dr. Jones, Acting Head of the Department of Hygiene, for permitting me the use of the Department's Laboratory of Bacteriology to make the fermentation tests, to Dr. Bates and Mr. Hovey, of the Forest Products Laboratories, for suggestions, and expecially to Mr. Hovey for making the cooks of pure Balsam Fir and Spruce.

SUMMARY.

1. A dozen representative Canadian sulphite liquors were analyzed, the results of which showed that the best liquors contained as high a percentage of sugar as those produced in Europe. These should yield at least 1 per cent of alcohol by volume, which is considered good practice in Europe.

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2. A rapid method for the estimation of sugar in the liquors has been proposed.

3. The Canadian liquors fall into two sharply defined classes. The one has about 20 per cent of its organic matter in the form of reducible sugars, and the other 28 per cent. Our experimental results show that this difference cannot be ascribed to a difference in the relative proportions of Spruce and Balsam being cooked, nor primarily to the strength of free acid used in the cook, nor to incomplete hydrolysis of the polysaccharides, but must be due to destruction of sugar in the cook.

4. The experimental results show further: (1) That the amount of sugar present does not reach a maximum; (2) That most of the sugar is produced before the end of the 7th hour; (3) That the temperature after the 7th hour is exceedingly important so far as the yield of sugar is concerned— the yield being very materially reduced if the temperature exceeds 145° C.; (4) That the first sugars to be destroyed are the fermentable ones.

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